

DRFT-IR Studies of the Surface of  $\gamma$ -Alumina

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**Abstract:**  $\gamma$ -Alumina surfaces dehydrated at 450 and 700 °C were studied by using the conventional pyridine adsorption-DRFTIR technique. Three types of Lewis acid sites are present on the surface, and in each case pyridine adsorbed on them is concomitantly interacting with their adjacent OH groups. Because only three types of Lewis acid sites are present, only three hydrogen bonding bands were observed upon pyridine adsorption. From correlation of OH bands with hydrogen bonding bands, it is found that weak Lewis acid sites have type II<sub>66</sub> or II<sub>64</sub> OH groups as their neighbors, medium strong Lewis acid sites have type III OH groups near by, and strong Lewis acid sites have type I<sub>6</sub> OH groups next to them. Dehydration at 700 °C generates more types of OH groups that also interact with pyridine. The reactivity of OH groups is not determined by their acidity and space restrictions, but rather by their proximity to Lewis acid sites. We assigned the three types of Lewis acid sites to five-, four-, and three-coordinate Al<sup>3+</sup> ions.

## Introduction

Aluminas of various forms are one of the most commonly used materials as catalysts and their supports.<sup>1</sup> Due to their responsibility for a wide range of catalytic reactions, properties of aluminas have been the subject of many investigations. At the same time, alumina surfaces may be the most complicated metal oxide model system among catalyst materials. Many attempts have been made over the past 40 years to assign the hydroxyl bands observed from IR spectroscopic studies and to understand the nature of the surfaces. Morterra and Magnacca<sup>2</sup> recently reviewed the field's progress. The assignments for hydroxyl spectral features and their changes upon dehydroxylation have been further examined very recently by Tsyganenko and Mardilovich.<sup>3</sup> They considered all possibilities of coordination that hydroxyls may have among different crystal planes at different stages of dehydroxylation. Their studies revealed that the types of hydroxyls on the surfaces of aluminas increase as dehydroxylation occurs.

Lewis acidity of aluminas is another extensively studied subject in this field. The Lewis acid sites are generated after dehydroxylation of the surfaces and present in the form of coordinatively unsaturated aluminum ions. A large body of studies on this aspect with a variety of techniques such as solid state NMR,<sup>4–7</sup> FT-IR,<sup>2,8–11</sup> and theoretical calculations<sup>12–15</sup> have revealed the presence of three-, four-, and five-coordinate Al

ions in aluminas as Lewis acid sites even though the results obtained from different techniques are not always consistent with each other. FT-IR spectroscopy has been shown to be unique for studying surface properties of aluminas. Our understanding of hydroxyl types and of surface coordinatively unsaturated Al sites is largely based on IR studies. From earlier IR work it has been known that alumina surface hydroxyls are very weak acids. Upon pyridine adsorption, no pyridinium ions are formed<sup>7</sup> and hydrogen bonding is the main interaction between surface hydroxyls and adsorbed molecules. Lewis acidity on alumina surfaces is also found to be complicated: three types of Lewis acid sites have been observed from CO and pyridine adsorption and assigned to three- and five-coordinate Al ions and Al<sup>3+</sup>–Al<sup>3+</sup> ion pairs.<sup>2,8,9,11</sup> Theoretical calculations<sup>12–15</sup> support the assignments for the three- and five-coordinate Al ions made in the IR studies. However, recent <sup>27</sup>Al NMR studies show that no three-coordinate Al site could be observed, only four- and five-coordinate Al ions are present in aluminas as Lewis acid sites.<sup>5</sup> This discrepancy between different methods obviously requires more work on this subject.

Despite a wealth of information about alumina surfaces, details of surface structures are still lacking. There are also unanswered questions about the nature of Lewis acid sites as just mentioned and the chemistry of the surface hydroxyls. Experimentally, up to or more than five types of surface hydroxyls have been observed for dehydrated aluminas, but only the ~3775 cm<sup>-1</sup> surface OH group is shown to be the most reactive.<sup>2</sup> This phenomenon cannot be explained by acidity alone.

In this paper, we report the results of studies of  $\gamma$ -alumina surfaces upon dehydration using the conventional pyridine adsorption/FT-IR spectroscopic technique. The results reported here provide a detailed picture of surface hydroxyl arrangement and surface Lewis acid sites, and also explain the reactivity of surface hydroxyls just mentioned. Assignments for Lewis acid sites probed by pyridine are also discussed.

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## Experimental Section

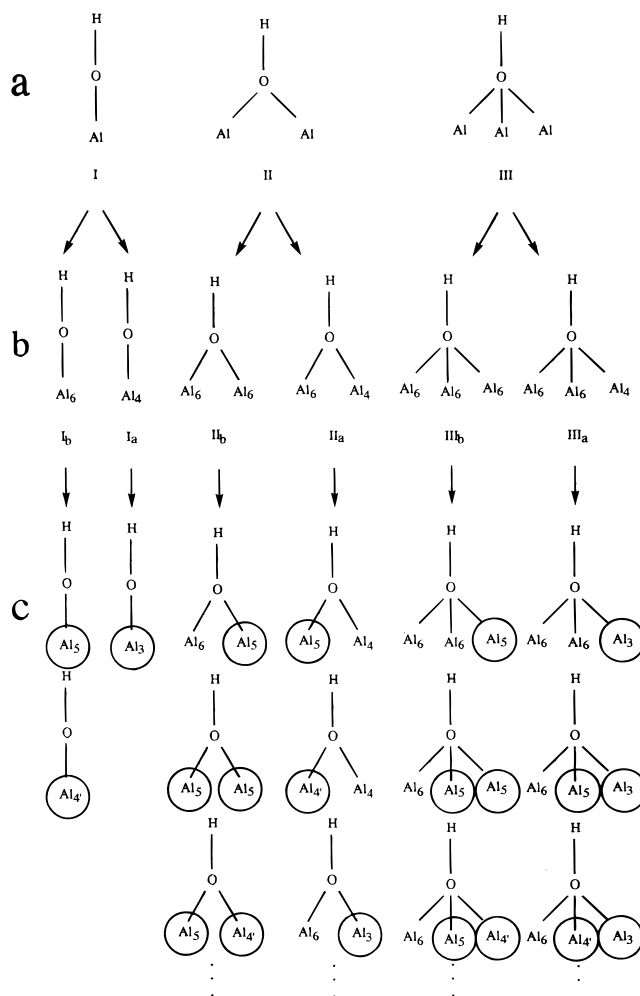
**Chemicals and Sample Preparations.** Pyridine was purchased from Aldrich and transferred from a newly opened bottle to a stainless steel bottle on the automation line (for adsorption and desorption) in a drybox under flowing dry  $N_2$ .  $\gamma$ -Alumina was a product (E-160) of Condea Chemie (surface area of calcined is  $160 \text{ m}^2/\text{g}$ ). The  $450^\circ\text{C}$  dehydrated  $\gamma$ -alumina was obtained in situ in the diffuse reflectance IR sample chamber (see below), while the  $700^\circ\text{C}$  dehydrated  $\gamma$ -alumina was obtained by calcining  $\gamma$ -alumina in an aluminum sample cup at  $700^\circ\text{C}$  for 2.5 h in air before quickly transferring it to the sample chamber followed by the same procedure as for the  $450^\circ\text{C}$  dehydration. The sample transfer procedure for the high-temperature dehydrated sample is due to the facility limitation in this laboratory and leads to re-adsorption of some moisture onto the sample which may not be completely removed by the later  $450^\circ\text{C}$  dehydration.

**Instruments and Procedures for Acidity Measurements.** Diffuse reflectance Fourier-transform infrared (DRFTIR) spectra were recorded on a Perkin-Elmer Paragon 1000PC spectrometer equipped with a MCT detector and a Spectra-Tech diffuse reflectance high-temperature chamber with KBr windows allowing gases such as  $N_2$  to flow through.  $\gamma$ -Alumina was ground into a fine powder with an agate mortar and transferred evenly into an aluminum sample cup. The samples were first dehydrated at  $450^\circ\text{C}$  for 1 h under flowing dry  $N_2$  ( $40 \text{ mL}/\text{min}$ ) and then cooled to room temperature. Pyridine vapor was introduced in a  $N_2$  stream for about 1 min, then shut off. The system was equilibrated at room temperature for 1 h under flowing  $N_2$ , allowing removal of physisorbed pyridine. Samples were then heated to  $180^\circ\text{C}$  under flowing  $N_2$  and maintained at this temperature for 1 h, then cooled to room temperature. Finally, the procedure was repeated at  $400^\circ\text{C}$ . Single beam spectra were collected at room temperature after heating with use of an automation program. For the single beam background spectrum, a fine ground KBr powder was used. The ratios of the sample spectra against the background spectrum were made, and the spectra were converted to Kubelka-Munk spectra after baseline and offset corrections. Difference spectra were obtained by subtracting the sample spectra without pyridine from those containing pyridine. Due to interactions of adsorbed pyridine with the surface, bands generated by adsorption are positive, while bands "removed" by adsorption are negative.

## Results and Discussion

**Models of Alumina Surface Hydroxyls.** The structure of  $\gamma$ -alumina is built by  $\text{AlO}_6$  octahedra and  $\text{AlO}_4$  tetrahedra. It has a slightly tetragonally distorted face-centered cubic lattice structure.<sup>10</sup> The exposed surface studied most in the literature<sup>2,3,9,10,16</sup> has (100), (110), and (111) crystal planes. The first model for the alumina surface was proposed by Peri in 1965.<sup>16</sup> Peri's model explained the five OH bands experimentally observed from IR spectroscopic studies of partially dehydroxylated aluminas. However, due to the inadequacy of Peri's model for the chemical properties of alumina surfaces,<sup>2</sup> several models were subsequently developed, as described in Figure 1. Figure 1a gives the model proposed by Tsyganenko and Filimonov<sup>17</sup> after studies of a large number of metal oxides including transition aluminas. According to this model, three types of hydroxyl groups are possible on the surface of aluminas and of other metal oxides. Hydroxyls can be coordinated by one, two, or three  $\text{Al}^{3+}$  ions.

Figure 1b gives the model by Knözinger and Ratnasamy<sup>10</sup> that distinguish tetrahedrally and octahedrally coordinated  $\text{Al}^{3+}$  ions. The types of surface hydroxyl groups are thus doubled in this model, each being split into two sub-types. Figure 1c shows the model proposed very recently by Tsyganenko and Mardilovich,<sup>3</sup> who considered other possible coordination of



**Figure 1.** Possible configurations of hydroxyls and Lewis acid sites on the surface of aluminas considered at different levels of complication: (a) model proposed by Tsyganenko and Filimonov; (b) model proposed by Knözinger and Ratnasamy; and (c) model proposed by Tsyganenko and Mardilovich. The Roman symbols used are according to Knözinger's notation. Circles represent possible Lewis acid sites.

$\text{Al}^{3+}$  ions upon surface dehydroxylation. Here, the types of hydroxyl groups are further increased. In addition to those shown in Figure 1, Busca et al.'s model<sup>18</sup> considered cation vacancies in transition aluminas.

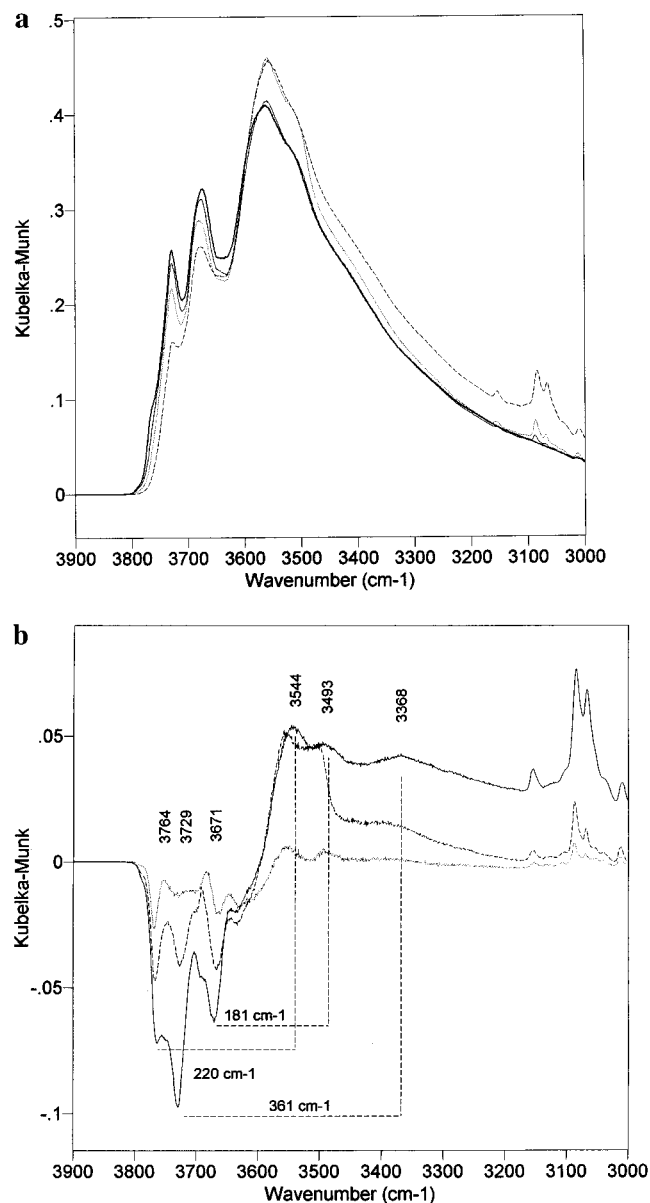
In Figure 1c, we add two things to the model: (1) an OH group coordinated by the four-coordinate  $\text{Al}^{3+}$  ion and (2) Lewis acid sites. The former distinguishes the newly formed four-coordinate  $\text{Al}^{3+}$  ions, generated by further dehydroxylation of five-coordinate  $\text{Al}^{3+}$  ions, from the original tetrahedrally coordinated  $\text{Al}^{3+}$  ions, while the latter describes possible configurations of coordinatively unsaturated  $\text{Al}^{3+}$  sites (Lewis acid sites). The presence of four-coordinate Lewis acid sites has been proposed by Coster et al.<sup>5</sup> on the basis of their  $^{27}\text{Al}$  high-resolution NMR studies of alumina adsorbed with ammonia, and recently Al Lewis acid sites in zeolites were also found to be four-coordinated.<sup>19</sup> Following these reports,<sup>5,19</sup> the model in Figure 1c shows that only three types of Lewis acid sites are possible on the surface of aluminas, corresponding to five-, four-, and three-coordinate  $\text{Al}^{3+}$  ions. If pairs of coordinatively unsaturated  $\text{Al}^{3+}$  ions are considered, as proposed by Morterra et al.,<sup>2,9</sup> more types of Lewis acid sites should be possible.

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(17) (a) Tsyganenko, A. A.; Filimonov, V. N. *Spectrosc. Lett.* **1972**, *5*, 477. (b) Tsyganenko, A. A.; Filimonov, V. N. *J. Mol. Struct.* **1973**, *19*, 579.

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**Figure 2.** (a) DRFTIR spectra of  $\gamma$ -alumina calcined at 450 °C for 1 h under flowing  $N_2$  (dark solid line) before pyridine adsorption; (dash line) pyridine adsorption at room temperature; and (dotted line) pyridine adsorption followed by heating at 180 °C for 1 h and (solid line) at 400 °C for 1 h. All spectra were recorded at room temperature. (b) Difference spectra of the sample in part a: (solid line) after – before, (dash line) 180 °C – before, and (dotted line) 400 °C – before.

The presence of five- and three-coordinate  $Al^{3+}$  Lewis acid sites seems easy to accept because, intuitively, (1) simple dehydroxylation of  $AlO_6$  octahedra and  $AlO_4$  tetrahedra in the alumina structure should generate them and (2) CO and pyridine adsorption<sup>2,9</sup> and theoretical calculations<sup>12–15</sup> have suggested their presence, while that of the four-coordinate  $Al^{3+}$  Lewis acid site is rather difficult to visualize without distinguishing between newly-formed four-coordinate  $Al^{3+}$  ions and the original tetrahedrally coordinated  $Al^{3+}$  ions. In the models reported in the literature,<sup>2,3,9,10,16–18</sup> no such distinction was made. Here we add the newly-formed four-coordinate  $Al^{3+}$  ions into the model because recent NMR studies<sup>5,19</sup> have suggested their presence.

**$\gamma$ -Alumina Dehydrated at 450 °C.** Figure 2a shows DRFTIR spectra of alumina dehydrated at 450 °C under flowing  $N_2$  and of room temperature pyridine adsorption followed by desorption at 180 and 400 °C. The spectrum before pyridine

adsorption exhibits bands at 3764, 3728, 3675, 3561, and 3512  $cm^{-1}$ . Following the literature assignment,<sup>2,3</sup> the 3764  $cm^{-1}$  band is associated with a type  $I_6$  OH group, the 3728- $cm^{-1}$  band with a type  $II_{66}$  OH group, and the 3675- $cm^{-1}$  band with a type III OH group. The 3561- and 3512- $cm^{-1}$  bands are due to hydrogen-bonded OH groups and some type of III OH groups may overlap with them, but are difficult to differentiate. Note that in the literature,<sup>2,3</sup> assignments for the bands are still under debate. However, more recent experimental results and theoretical calculations<sup>3,20,21</sup> tend to suggest that hydroxyl band wavenumbers follow the sequence of  $I_4 > I_6 > II_{66} > II_{64} > III$ .

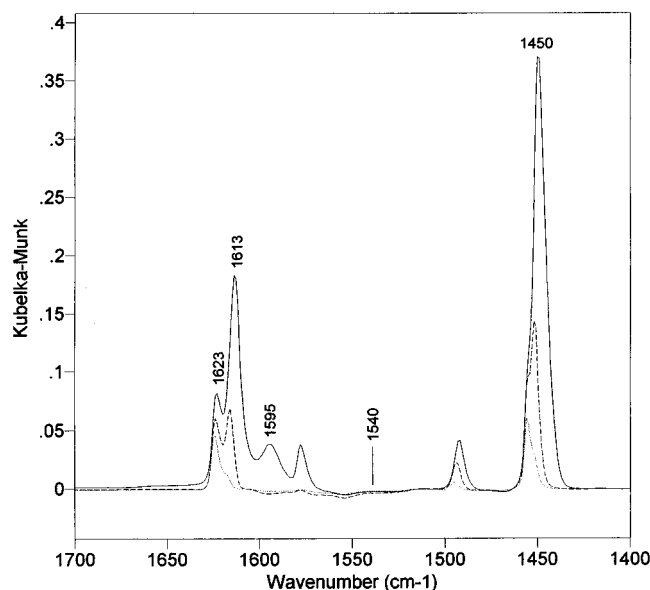
After pyridine adsorption, two major spectral changes are observed: (1) a decrease in intensity of bands at 3764, 3728, and 3675  $cm^{-1}$ , and (2) an increase in intensity of those at 3561 and 3512  $cm^{-1}$ , together with appearance of a broad band around 3370  $cm^{-1}$ . The intensity decrease of the bands at 3764, 3728, and 3675  $cm^{-1}$  indicates that interactions between pyridine and OH groups have taken place, and the intensity increase of the bands at 3561 and 3512  $cm^{-1}$  and the appearance of the band at 3370  $cm^{-1}$  suggest that hydrogen bonding has formed. The latter confirms the assignment for the bands at 3561 and 3512  $cm^{-1}$  to hydrogen-bonded species.

Difference spectra more clearly show the changes of surface hydroxyls upon pyridine adsorption. Figure 2b gives difference spectra before and after pyridine adsorption at room temperature, thermally treated at 180 and 400 °C. From the room temperature spectrum (solid line), it is seen that three bands are “removed” by pyridine (the negative bands) and three other bands are formed (the positive bands). At a first glance, it seems reasonable to correlate the three “removed” bands to the three newly formed bands in order of decreasing wavenumbers because hydrogen bonding should “move” the most acidic OH groups to smaller wavenumbers. However, this is not seen after temperature studies were conducted. The dashed and dotted line spectra in Figure 2b are spectra of samples treated at 180 and 400 °C, respectively, after pyridine adsorption. It is seen from the spectra (compare the relative intensity of the bands) that after the 180 °C heat treatment, the 3729- and 3368- $cm^{-1}$  bands dramatically decreased, suggesting that these two bands are related. From relative band intensities, correlation of the 3764- $cm^{-1}$  band to the 3544- $cm^{-1}$  band and the 3671- $cm^{-1}$  band to the 3493- $cm^{-1}$  band can be made. Further heat treatment at 400 °C confirms this correlation. The 3729- and 3368- $cm^{-1}$  bands disappeared completely, and the 3764- and 3671- $cm^{-1}$  bands were significantly decreased, as were the 3544- and 3493- $cm^{-1}$  bands. From this correlation, it is clear that pyridine adsorption shifts the 3764-, 3729-, and 3671- $cm^{-1}$  bands by 220, 361, and 181  $cm^{-1}$ , respectively, through  $OH \cdots pyridine$  hydrogen bonding. These results obviously contradict a general understanding about OH group acidity that the lower the wavenumber of OH groups, the stronger the acid strength, and the more band shift toward lower wavenumbers by hydrogen bonding.<sup>2,10</sup> To understand this phenomenon, IR spectra of the sample in the pyridine absorption region were examined.

Figure 3 shows difference IR spectra of the sample in the spectral region 1700–1400  $cm^{-1}$ . The three spectra correspond to room temperature and 180 and 400 °C treated samples after pyridine adsorption (see figure caption). The absence of a band at  $\sim 1540$   $cm^{-1}$  indicates that there are no Brønsted acid sites on the surface strong enough to form pyridinium ions. The presence of a 1450- $cm^{-1}$  band demonstrates the presence of

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**Figure 3.** DRFTIR spectra of the same sample in the spectral region 1700–1400  $\text{cm}^{-1}$ . Labels are the same as those in Figure 2b.

Lewis acid sites. The multiplicity of the band indicates that more than one type of Lewis acid site with different acid strengths exists. These results are consistent with those reported in the literature.<sup>2,8</sup> The different Lewis acid sites are more clearly seen in the spectral region 1630–1560  $\text{cm}^{-1}$ . Detailed assignment for bands in this region can be found in the discussion by Morterra et al.<sup>2,10</sup> Following Morterra et al.,<sup>2,10</sup> it is known that no physisorbed pyridine molecules are present on the surface of alumina, and only pyridine adsorbed on weak (band at 1595  $\text{cm}^{-1}$ ), medium strong (band at 1613  $\text{cm}^{-1}$ ), and strong (band at 1623  $\text{cm}^{-1}$ ) Lewis acid sites is present. From this result, it is concluded that OH groups are not disturbed by physisorbed pyridine, but by the pyridine adsorbed on the Lewis acid sites.

Due to the concomitant interactions of pyridine with two centers, the strength of hydrogen bonding between OH groups and Lewis acid adsorbed pyridine should depend on the remaining pyridine charge after it is adsorbed on Lewis acid sites. Based on the facts that interactions of pyridine with Lewis acid sites are through its N-lone pair electrons and that pyridine ring charge would flow toward the N center due to acid–base interactions, it is expected that the stronger the acid strength of Lewis acid sites, the smaller the remaining charge on pyridine, and the weaker the hydrogen bonding interactions with adjacent OH groups. Following temperature effects and correlating the bands in hydroxyl and pyridine spectral regions, it is clear that pyridine adsorbed on the weak Lewis acid sites is interacting with the 3729- $\text{cm}^{-1}$  (type  $\text{II}_{66}$ ) OH groups, pyridine adsorbed on the medium strong Lewis acid sites are interacting with the 3671  $\text{cm}^{-1}$  (type III) OH groups, and pyridine on the strong Lewis acid sites is interacting with the 3764- $\text{cm}^{-1}$  (type  $\text{I}_6$ ) OH groups. Because of the simultaneous interactions of pyridine with both Lewis acid sites and OH groups, the OH groups therefore must be located adjacent to the Lewis acid sites.

The observed irregular shift phenomenon of OH bands after pyridine adsorption can now be rationalized. Pyridine molecules adsorbed on weak Lewis acid sites interact relatively strongly with adjacent OH groups, leading to a large bathchromic shift of the OH band. Pyridine molecules adsorbed on medium and strong Lewis acid sites interact relatively weakly with adjacent OH groups, giving rise to smaller bathchromic shifts of the OH band.

The very similar behavior of the 3760- and 3671- $\text{cm}^{-1}$  bands upon desorption implies that interactions between pyridine and these two types of OH groups are not so different. The similar band shifts, 220 versus 181  $\text{cm}^{-1}$ , for these two types of OH groups reflect this point. It is therefore concluded that medium and strong Lewis acid sites on alumina have similar strength.

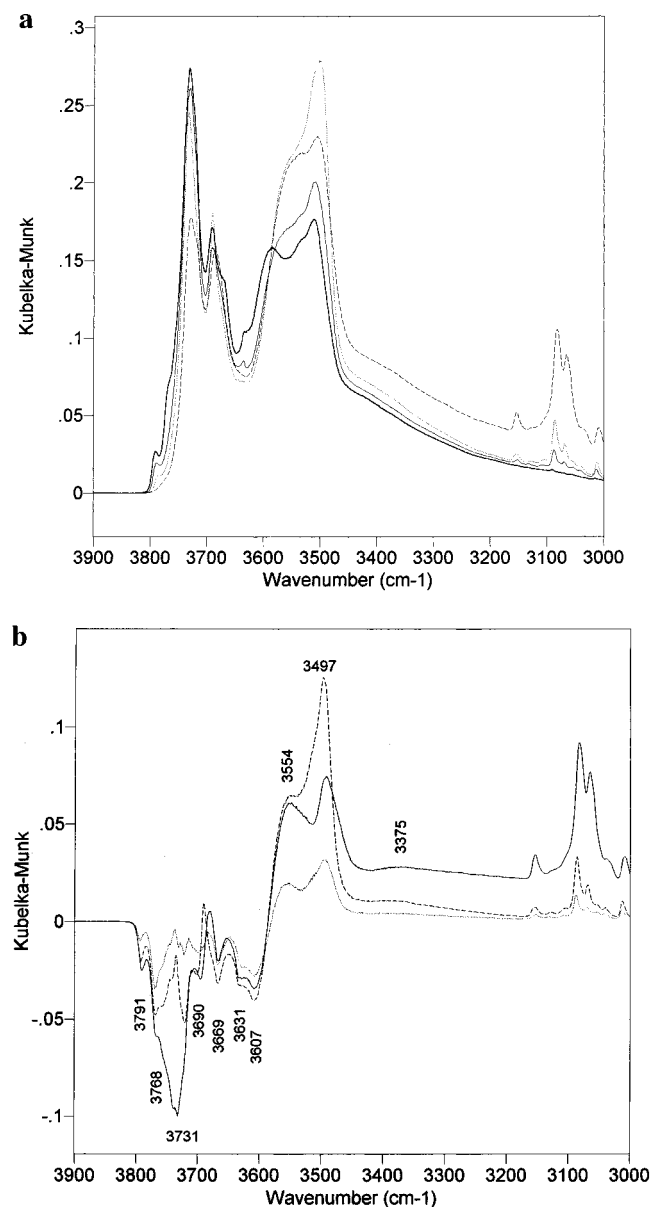
From the above results, the reason the type  $\text{I}_6$  OH groups are the most reactive<sup>2</sup> is understood. Because they are located next to the strongest Lewis acid sites, base molecules adsorbed on the Lewis acid sites are concomitantly interacting with them. If experimental conditions are not sufficient enough to remove pyridine from the strongest Lewis acid sites, disturbance of the type  $\text{I}_6$  OH groups will remain. It is well-known that the most persistent sites to desorption on the surface are the strongest Lewis acid sites.  $\text{I}_6$  OH groups are, therefore, the most disturbed by pyridine. The superior reactivity of the type  $\text{I}_6$  OH group over other OH groups on the surface is not due to their chemical property differences or easy access by base molecules as suggested by Morterra and Magnacca.<sup>2</sup> It is simply due to their close proximity to the strongest Lewis acid sites.

**$\gamma$ -Alumina dehydrated at 700 °C.** Figure 4a shows DRFT-IR spectra of alumina dehydrated at 700 °C for 2.5 h in air followed by heating at 450 °C for 1 h under flowing dry  $\text{N}_2$  in the diffuse reflectance IR chamber. Compared to the spectra of 450 °C treated alumina (spectra a and b, Figure 2), the 700 °C treated sample contains more types of OH groups. Bands at 3791 and 3768  $\text{cm}^{-1}$  are due to  $\text{I}_4$  and  $\text{I}_6$  OH groups. Bands at 3731 and 3690  $\text{cm}^{-1}$  are due to  $\text{II}_{66}$  and  $\text{II}_{64}$  OH groups, while those at 3669, 3631, and 3607  $\text{cm}^{-1}$  are due to type III OH groups. However, these assignments can only be considered to be idealized because, as discussed by Tsyganenko and Mardilovich,<sup>3</sup> a variety of OH groups different in number and aluminum coordination are present on the surface as a result of further dehydroxylation. During sample transfer, some moisture re-adsorbed onto the sample, producing hydrogen-bonded OH groups with bands around 3550  $\text{cm}^{-1}$ .

Adsorption of pyridine results in disappearance of the bands at 3791 and 3768  $\text{cm}^{-1}$ , and dramatically decreases the  $\sim 3731$ - $\text{cm}^{-1}$  band. Bands at 3690 and 3669  $\text{cm}^{-1}$  are slightly disturbed, while those around 3550  $\text{cm}^{-1}$  are increased and become centered at 3561 and 3504  $\text{cm}^{-1}$ . A weak broad band around 3378  $\text{cm}^{-1}$  is also generated.

Difference spectra of the samples show more clearly the removal and generation of bands upon pyridine adsorption. Figure 4b shows difference spectra of samples after pyridine adsorption at room temperature and desorbed at 180 and 400 °C. Four features are seen from the spectra: (1) more types of OH groups are produced after 700 °C treatment (they are all disturbed by pyridine); (2) there are still three types of hydrogen-bonded bands at 3554, 3493, and 3375  $\text{cm}^{-1}$ ; (3) the most easily removed pyridine molecules are those interacting with type  $\text{II}_{66}$  and type  $\text{II}_{64}$  OH groups; and (4) after 180 °C desorption, intensities of the bands at 3667, 3631, and 3607  $\text{cm}^{-1}$ , as well as that at 3497  $\text{cm}^{-1}$ , increase.

The first feature, consistent with that reported by Tsyganenko and Mardilovich,<sup>3</sup> indicates the generation of more types of OH groups, as shown in Figure 1c. The second feature confirms the presence of only three types of Lewis acid sites on the surface. If more types of Lewis acid sites were present after high-temperature dehydroxylation, more hydrogen-bonded bands would be observed. This feature also confirms that hydrogen bonding between pyridine and OH groups is indeed determined by the acid strength of Lewis acid sites, not by the acidity of OH groups. The third feature demonstrates that Lewis acid sites are still in the proximity of OH groups, and that the feature of



**Figure 4.** (a) DRFTIR spectra of  $\gamma$ -alumina calcined at 700 °C for 2.5 h in air and then at 450 °C for 1 h under flowing  $N_2$  (dark solid line) before pyridine adsorption; (dash line) pyridine adsorption at room temperature; (dotted line) pyridine adsorption followed by heating at 180 °C for 1 h and (solid line) at 400 °C for 1 h. All spectra were recorded at room temperature. (b) Difference spectra of the sample in part a: (solid line) after – before, (dash line) 180 °C – before, and (dotted line) 400 °C – before.

the arrangement of surface Lewis acid sites and OH groups still exists after a high-temperature treatment. The last feature supports the band correlation and assignments, but detailed explanation of the phenomenon requires further study. One possibility is migration of some adsorbed pyridine from weak Lewis acid sites to strong Lewis acid sites during heat treatment. Migration of surface adsorbed pyridine upon heating has been observed in other microporous systems.<sup>22</sup>

As shown in the previous<sup>23,24</sup> and present pyridine adsorption studies, the surface of alumina contains only three types of Lewis

acid sites. The present observations of three hydrogen-bonding bands after pyridine adsorption provide strong evidence for this. Along with the model given in Figure 1c showing only three types of coordination possible for Lewis acidity, and the experimental evidence provided by other techniques such as  $^{27}Al$  NMR for the presence of Lewis acid sites with four coordination,<sup>5,19</sup> we assign the three Lewis acid sites observed in the present study on  $\gamma$ -alumina to five-, four-, and three-coordinate  $Al^{3+}$  ions in order of increasing acid strength.

From the results obtained in this study, it appears that all types of Lewis acid sites on the surface of  $\gamma$ -alumina are surrounded by OH groups. This kind of arrangement of OH groups and Lewis acid sites on alumina is really intriguing and implies that migration of protons or OH groups must be taking place during dehydration. Indeed, proton/OH migration on  $\gamma$ -alumina surface during dehydration has been proposed by Huggins and Ellis in their  $^{27}Al$  NMR studies.<sup>25</sup> Our results are experimental evidence for this mechanism.

Similar results were also obtained for other  $\gamma$ -aluminas prepared in different ways. This suggests that the results presented here reflect a general feature of surface structure of this type of alumina.

## Conclusions

Studies of the surface of  $\gamma$ -aluminas dehydrated at different temperatures with the conventional pyridine adsorption-DRFTIR technique have revealed their very important surface structure features. Surface hydroxyls and Lewis acid sites are adjacent to each other. The weak Lewis acid sites have type  $II_{66}$  or type  $II_{64}$  OH groups as neighbors, the medium strong Lewis acid sites have type III OH groups near by, while the strong Lewis acid sites have type  $I_6$  OH groups next to them. Due to the proximity of OH groups and Lewis acid sites on the surface, interaction of OH groups with adsorbed species is not determined by the OH group acidity itself or by their space accessibility, but by the strength of the Lewis acid sites. The puzzling phenomenon that type  $I_6$  OH groups are the most reactive toward adsorbed species is now understood. The location of this type of OH group adjacent to the strongest Lewis acid site provides it opportunity to interact preferentially with adsorbed molecules.

Our results also demonstrate that the three types and strengths of Lewis acid sites correspond to the three possible  $Al^{3+}$  coordination configurations predicted in the model given in Figure 1c. The five-coordinate  $Al^{3+}$  sites are weak Lewis acid sites, while the three- and four-coordinate  $Al^{3+}$  sites are strong and medium strong Lewis acid sites. The difference in acid strength between the latter two is not as significant as that between the weak (five-coordinate) and strong (three-coordinate) Lewis acid sites.

The observation of Lewis acid sites close to hydroxyls on the surface of  $\gamma$ -alumina provides experimental evidence for migration of protons/OH groups on the surface during dehydration.

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